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Formation of Porous Germanium Layers by Silver-Ion Implantation

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Abstract—We propose a method for the formation of porous germanium (*P*-Ge) layers containing silver nanoparticles by means of high-dose implantation of low-energy Ag^+ ions into single-crystalline germanium (*c*-Ge). This is demonstrated by implantation of 30-keV Ag^+ ions into a polished *c*-Ge plate to a dose of 1.5×10^{17} ion/cm^2 at an ion beam-current density of 5 μA/cm^2. Examination by high-resolution scanning electron microscopy (SEM), atomic-force microscopy (AFM), X-ray diffraction (XRD), energy-dispersive X-ray (EDX) microanalysis, and reflection high-energy electron diffraction (RHEED) showed that the implantation of silver ions into *c*-Ge surface led to the formation of a *P*-Ge layer with spongy structure comprising a network of interwoven nanofibers with an average diameter of ~10–20 nm Ag nanoparticles on the ends of fibers. It is also established that the formation of pores during Ag^+ ion implantation is accompanied by effective sputtering of the Ge surface.

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Porous germanium (*P*-Ge), which was experimentally observed and described for the first time in [1], is now widely used in opto-electronics. Together with silicon, *P*-Ge is a base material for solar cells [2]. Various technologies have been developed for the formation of *P*-Ge layers, including electrochemical etching of single-crystalline germanium (*c*-Ge) in concentrated electrolytes [3], plasma-assisted chemical-vapor deposition [4], spark-discharge processing [5], and thermal annealing of GeO_2 films in hydrogen [6].

An especially interesting effective method of obtaining thin nanodimensional *P*-Ge layers on a germanium surface is based on its high-dose irradiation with various ions in vacuum. To the best of the authors' knowledge, the first report on the appearance of *P*-Ge structure on *c*-Ge surface upon implantation of 50-keV Ge^+ ions was presented in [7]. Later, the porous structure was repeatedly observed (see, e.g., review [8]) in amorphous germanium (*a*-Ge) and *c*-Ge upon the implantation of various low- and high-energy (>1 MeV) ions including Ga^+, Ge^+, Mn^+, Ni^+, In^+, Sn^+, Sb^+, I^+, Au^+, and Bi^+. Note that the implantation of Ag^+ ions for obtaining *P*-Ge layers on the open Ge surface has not been reported until now.

To increase the absorption of solar energy by semiconductor elements, it was proposed [9, 10] to introduce metal nanoparticles into their structure. Under the action of light, these nanostructures exhibit localized plasmon resonance that is manifested by intense absorption of light by, e.g., Ag and Au nanoparticles in the visible spectral range [11, 12], providing a total contribution to enhanced optical absorption of a thin semiconductor layer containing these metal nanoparticles. Moreover, a local electromagnetic field arising in the vicinity of nanoparticles due to the plasmon resonance is capable of generating electron–hole pairs in semiconductors [10]. In practice, the first implementation of a *P*-Ge based composite material with electrochemically synthesized Au nanoparticles in the porous structure was reported in [13].

In this Letter, we propose a new approach to obtaining open surface *P*-Ge layers simultaneously with the synthesis of Ag nanoparticles inside them, which consists in high-dose implantation of low-energy Ag^+ ions into *c*-Ge plates.

The samples of structured composite material with *P*-Ge layer were prepared on 0.5-mm-thick polished *c*-Ge substrates. These substrates were implanted at a temperature of 25°C with 30-keV Ag^+ ions to a dose of 1.5×10^{17} ion/cm^2 at an ion beam-current density of 5 μA/cm^2 on an ILU-3 linear ion accelerator. The morphology of the structured surface layers and microanalysis of the ion-implanted Ge layer were studied in a Merlin (Carl Zeiss) high-resolution scanning electron microscope equipped with a reflection high-energy electron-diffraction (RHEED) attach-